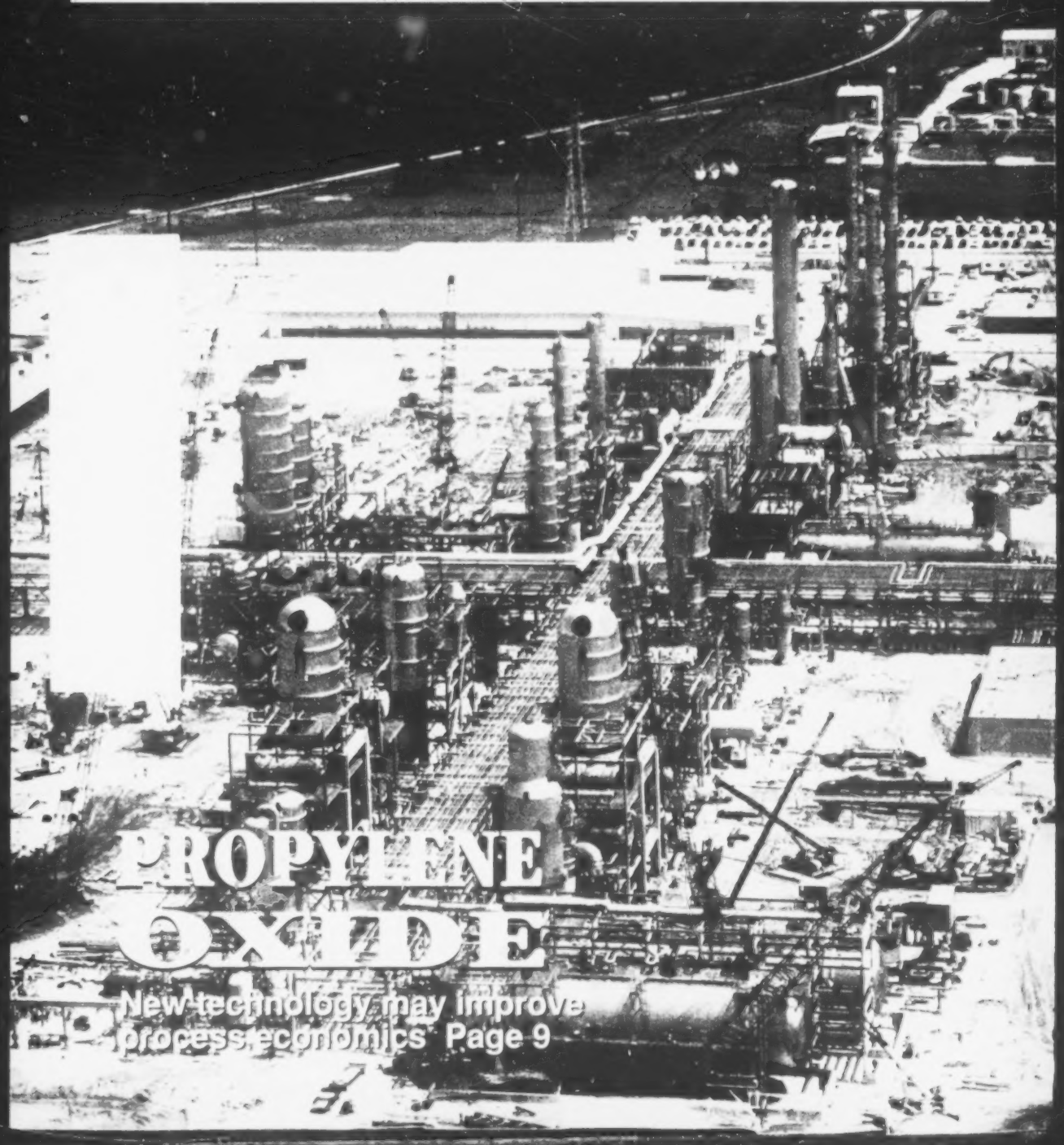
CHEMICAL & ENGINEERING NEWS

C&EN

MARCH 2, 1992

FINAL PROGRAM – ACS NATIONAL MEETING IN SAN FRANCISCO PAGE 33



PROPYLENE OXIDE

New technology may improve process economics Page 9

CHEMICAL & ENGINEERING NEWS

C&EN

MARCH 2, 1992

News of the Week

- Systematic studies of silicone breast implants are likely to be undertaken, following recommendation by FDA advisory panel to keep implants on market, but under strict limits and monitoring. Page 4
- New policy on biotechnology products calls for regulating them on same basis as conventional products—on their risk, not on how they are made. Page 5
- Pure Air, a joint venture formed by Air Products and Mitsubishi to sell flue gas desulfurization technology, is offering to trade pollution rights for sulfur dioxide emissions as part of its market strategy. Page 6
- Solving environmental problems and achieving sustainable development won't be possible without stabilizing world population, warns a joint report of the U.S. National Academy of Sciences and the Royal Society of London. Page 6

COVER: Arco Chemical's new propylene oxide plant at Channelview, Tex., is scheduled to start up later this year.

Volume 70, Number 9
CENEAR 70 (9) 1–154
ISSN 0009-2347

BUSINESS

Chemical industry hopes to salvage its plan for lowering and harmonizing tariffs in the current Uruguay round of multilateral trade negotiations. Page 13

GOVERNMENT

Tenth edition of "Science & Engineering Indicators" takes a more international approach in its report and analysis of statistics pertinent to these two disciplines. Page 16

Group of past NSF Presidential Young Investigator awardees calls for more support for college teachers in effort to improve science literacy. Page 17

U.S., Russia, and Germany form international science and technology center aimed at employing former Soviet weapons scientists on nonmilitary projects in effort to thwart researchers' possible collaboration with Third World nations or terrorists. Page 18

SCIENCE/TECHNOLOGY

The seven resource centers of Caltech's Beckman Institute allow interdisciplinary research in the fields of chemistry, biology, materials science, and polymer science. Page 23

Funding for a massively parallel supercomputer to advance the field of structural biology is being sought through a grand challenge grant proposal. Page 25

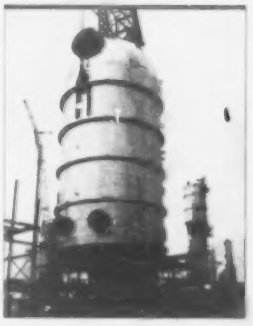
ACS NEWS

Council will consider two petitions to amend the bylaws next month in San Francisco; one on committee restructuring is likely to generate a good deal of debate. Page 26

FINAL PROGRAM

ACS spring meeting in San Francisco will be the largest national meeting ever, featuring over 6200 papers; exposition will comprise about 425 booths. Page 33

COVER STORY



Improved processes are helping propylene oxide producers keep their businesses healthy, but new plants and producers entering the market threaten to create overcapacity for the chemical. Page 9

LETTERS 2

CONCENTRATES

Business 7

Government 15

Science/Technology 22

THE DEPARTMENTS

Awards 139

Newscripts 154

Chemical & Engineering News
1155—16th St., N.W., Washington, D.C. 20036

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Published by
AMERICAN CHEMICAL SOCIETY
(202) 872-4600; TDD (202) 872-4432
John Kistler Crum, Executive Director
Robert H. Marks, Director, Publications Division

PUBLISHING BOARD: Ned D. Heindel (*Chairman, Board of Directors Chairman*), Joseph A. Dixon, *President*; Ernest L. Eliel, Richard L. Deming, Judith C. Giordan, William P. Jencks, and Gary J. Long

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Subscription Rates 1992: Printed editions: nonmembers U.S. 1 yr. $105, 2 yr. $189; outside U.S. 1 yr. $141, 2 yr. $261. Air freight rates available on request. Rates above do not apply to nonmember subscribers in Japan, who must enter subscription orders with Maruzen Co. Ltd., 3-10 Nihonbashi 2-chome, Chuo-ku, Tokyo 103, Japan. Tel: (03) 272-7211. Single copies: Current $15. Rates for back issues and volumes are available from Microforms & Back Issues Office, ACS, 1155—16th St., N.W., Washington, D.C. 20036. Back and current issues available on microfilm and microfiche. Rates on request from Microform Program, ACS.

Chemical & Engineering News (ISSN 0009-2347) is published weekly except for the last week in December by the American Chemical Society at 1155—16th St., N.W., Washington, D.C. 20036. Second-class postage paid at Washington, D.C., and additional mailing offices. POSTMASTER: Send address changes to Chemical & Engineering News, Membership & Subscription Services, P.O. Box 3337, Columbus, Ohio 43210. ACS assumes no responsibility for the statements and opinions advanced by the contributors to its publications.

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LETTERS

Earlier work on bromoaromatics

In a Science/Technology Concentrates section (C&EN, Jan. 13, page 20), attention was given to our recent article in the *Journal of Organic Chemistry* on hypochlorite-induced replacement of aromatic bromine by chlorine. I have just been made aware of relevant work accomplished by O'Connor and Burrows [*J. Org. Chem.*, **56**, 1344 (1991)], which should have been cited in our paper.

The latter described efficient, nickel(II) complex catalyzed aryl-halogen exchange (including quantitative conversion of C_6H_5Br to C_6H_5Cl in 30 minutes) using NaOCl. (In contrast, only 1 to 2% production of C_6H_5Cl from C_6H_5Br was observed in the absence of Ni(II) catalyst.) The O'Connor/Burrows paper describes a breadth of synthetic utility for the Ni(II) catalyzed system and includes a noteworthy mechanistic discussion. We thank Burrows for bringing her work to our attention.

R. G. Landolt
Texas Wesleyan University, Fort Worth

Supercritical water oxidation

We were pleased to see the attention given to supercritical water oxidation in the special report by Robert W. Shaw et al. (C&EN, Dec. 23, 1991, page 26). However, we do not feel that the report fully reflects the progress that has been made in this field in the private sector.

ABB Lummus Crest Inc. became the worldwide, exclusive licensor of the Modar supercritical water oxidation technology in 1989. We have now completed two years of intensive engineering development on the process in collaboration with Modar Inc. Specific areas that required focused engineering development included process design and scaleup of the oxidation reactor, control of (sticky) precipitating salts, corrosion and materials of construction for the reactor and downstream equipment, mechanical design of the reactor and other high-pressure equipment, and integration of the process into a safe, environmentally acceptable system. It was necessary in this development to evaluate limitations and constraints imposed by materials and mechanical design, as well as to consider normal process concerns.

The above efforts have progressed far enough to proceed with the next step of designing and constructing a supercritical water oxidation demonstration plant. ABB Lummus Crest is actively pursuing opportunities for such a facility.

Herbert E. Barner
Technology Development Manager
ABB Lummus Crest Inc.
Bloomfield, N.J.

I have read with interest the special report on supercritical water. There are several statements that require clarification to describe more correctly the status of development of supercritical water oxidation technology.

Our company, Modar Inc., has been developing supercritical water oxidation processes for the destruction of hazardous aqueous wastes containing organics since the early 1980s. The original process patents, as well as several other subsequent patents from employee inventors, are all property of Modar Inc.

In the middle to late 1980s, Modar conducted two pilot-scale field tests, successfully processing hundreds of gallons per day of wastes containing polychlorinated biphenyls, priority pollutants, and the effluents from a pharmaceutical manufacturer. Beginning in October 1991, the U.S. Department of Energy, Stone & Webster Engineering Corp., and Modar have been undertakening an 18-month pilot-scale program aimed at treating 500 gal per day of wastes containing halogenated organics and substantial quantities of inorganic salts.

In 1989, ABB Lummus Crest of Bloomfield, N.J., became the worldwide, exclusive licensor of the Modar technology. After two years of engineering development, the process is ready for large-scale demonstration.

William R. Killilea
Vice President
Modar Inc., Natick, Mass.

Nutrient-based treatments

Burton Kallman's letter (C&EN, Dec. 2, 1991, page 4) is important in drawing attention to the neglect of nutrient-based procedures for treatment and prevention of diabetes, relative to the use of drugs. Trouble is, the drug industry is really only interested in chemotherapeutic agents for which they can get strong patents, and that tends to exclude nutri-

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Propylene Oxide Producers Look for Ways To Counter Sluggish Market

■ ***Process improvements may lower production costs, but overcapacity threatens as new plants, producers enter business***

Susan J. Ainsworth, C&EN Houston

The U.S. propylene oxide market is experiencing some serious growing pains, and producers are actively taking precautions to ensure that their businesses remain healthy. The industry is seeing new technologies that may lower the cost of production, but at the same time, new producers and plants are contributing to the possibility of capacity vastly outstripping demand during the mid- to late-1990s.

Arco Chemical, with the newest plant, is probably studying these changes as intensely as anyone in the chemical industry. Sometime in the third quarter of this year, the company plans to start up a world-scale plant to produce both propylene oxide and styrene via the ethylbenzene peroxidation process at its Channelview, Tex., complex. The plant will have capacity to produce 500 million lb of propylene oxide and 1.13 billion lb of styrene annually.

For many years Arco Chemical and Dow Chemical have shared the propylene oxide market in the U.S. exclusively, each claiming about half of the business. The chemical is used primarily to make urethane polyols and propylene glycol. But last June, Texaco Chemical announced its intent to enter the market as a third producer, with a new plant to produce propylene oxide and methyl *tert*-butyl ether (MTBE) coproducts using the isobutane peroxidation process to go on stream in early 1994.

In addition, Dow Chemical is considering using lime instead of caustic soda in its chlorohydrin process for making propylene oxide. This likely would improve its cost position and free up a significant amount of its caustic for merchant sales. Another factor making the U.S. propylene oxide market less friendly is the recession, which has deflated demand for propylene oxide and some of its coproducts, such as styrene, and for end-use products such as flexible and rigid foams for furniture and auto seats.

Although unfavorable market conditions and increased competition may have a negative effect on all U.S. propylene oxide producers, Arco Chemical and some industry observers believe that the company is best positioned to meet these challenges. That's because the company has the best cost position, a wealth of experience in operating propylene oxide plants, and equity partners to ease the burden of its coproduct styrene business.

It is tough for anyone to predict when propylene oxide demand will rebound. The market for propylene oxide is closely tied to the gross national product because it goes toward the production of "big-ticket consumer items such as automobiles and home furnishings," says Ronald L. Gist, a senior consultant at Pace Consultants in Houston.

Growth in propylene oxide may be buoyed by growth in demand for two key end uses—urethane polyols, which are used to make both flexible and rigid urethane foams used in automobiles, furniture, and bedding products; and propylene glycol, used in the production of unsaturated polyester resins for reinforced plastics, humectants for tobacco and food products, and for solvents used in the cosmetics industry.

"When the economy grows fairly robustly, propylene oxide grows a little faster than the economy," Gist says. On the other hand, "when there is a downturn, big-ticket items drop lower on a consumer's priority list, and propylene oxide grows slower than the GNP," he adds. Gist estimates that propylene oxide demand in the U.S. dropped less than 1% in 1991, but that it will grow about 1.5% between 1991 and 1992 and 2.6% per year in the mid-1990s.

Arco Chemical's forecast is brighter. From now through the mid-1990s, the company expects use of propylene oxide to grow 4% per year and that of styrene 3% per year in the U.S. Worldwide, the company predicts that propylene oxide

Crane lifts concentrator drum into place at Arco Chemical's Channelview, Tex., propylene oxide unit

will grow 6% per year and styrene 4% per year through the middle of this decade.

Still, increases in consumption of propylene oxide probably won't compensate for the planned jump in production. Propylene oxide operating rates in the U.S. are now holding at about 85%, but that will likely drop to roughly 65 to 70% in 1994 when Texaco's capacity comes on stream, says Michael Horvath Jr., a petrochemical consultant with Petrocon Associates in Houston. "There is absolutely not enough room for another plant in this market right now."

Indeed, the market has changed significantly since Arco Chemical broke ground for its plant in June 1990. "The lead time it takes to start up a plant of this size is tremendous," says Joseph T. Lee, manager for projects and development at Arco Chemical. "Our first authorization for spending was back in 1988 when the market was robust, demand was strong, and everybody in the industry was operating near capacity."

When Arco Chemical decided to build the new plant, it considered two in-house peroxidation routes to propylene oxide. One starts with isobutane and gives a *tert*-butyl alcohol (TBA) coproduct, which can be converted to the gasoline additive MTBE. The other route, which the company eventually decided on, starts with ethylbenzene and produces coproducts propylene oxide and α-methylbenzyl alcohol, which can be dehydrated to styrene. Arco Chemical says it was not easy to decide between the two processes. Unfortunately, it is not technically feasible to operate a propylene oxide plant on a swing basis such that either of the two coproducts can be produced to satisfy demand fluctuations. "We thought both were relatively good investments," recalls Lee.

Arco Chemical chose the propylene oxide/styrene process because it would give it a better coproduct balance for styrene and MTBE in its worldwide market, says Lee. All of its European propylene oxide operations and two thirds of its U.S. propylene oxide operations are MTBE-based. The company did not want to be "weighted on that one technology" too heavily, he adds. On the other hand, "we think that styrene is a viable long-term business, and we are well positioned to operate within it."

Since those big decisions were made, "we've had to try to forecast where the industry and the overall economy were going to go." Arco Chemical, Lee adds, "anticipated a recovery some time in 1991 and it did not materialize."

Nevertheless, the company maintains that its investment in the new plant was necessary to position itself to meet its customers' needs into the future. "There's always going to be swings up and down [in demand], but we have a responsibility to our customers to guarantee that we can get materials to them," Lee says.

Horvath says that although lower operating rates will hurt all three propylene oxide producers, Arco Chemical will likely weather the storm best. Lee says, "We think the new Channelview unit will have the best [ratio of] capital per pound of product produced for this technology. It will probably be the most energy efficient plant of any of the propylene oxide–styrene units we have built. And because this is our newest plant, it is, environmentally, the tightest plant we have built."

Experience in building and operating propylene oxide plants is one factor that Arco Chemical has on its side. The company has been producing propylene oxide via the peroxidation process since the late 1960s, when it built its first such plant at Bayport, Tex. It has since fine-tuned its technology while building each of its nine propylene oxide plants around the world.

"There have been a lot of changes in just physical equipment alone," says Donald P. Mykytiuk, director of project management at Arco Chemical. Process improvements have evolved over time and with each new plant, and the older plants have been retrofitted to continually bring them up to date.

The construction strategy for the new plant involved off-site fabrication whenever possible to cut costs, says construction manager John T. Casey. For instance, Arco Chemical had two oxidizers fabricated and brought from Japan to the plant site, notes Mykytiuk. It also modularized the pipe racks for the plant and brought the units in by truck and barge.

With the expertise and technology improvements that Arco Chemical has honed over the years, "we now can get superior yields and efficient production out of smaller pieces of equipment," says Terry L. Stierman, technical superintendent at the new plant. "We've learned how to spend less capital but still get the best cost efficiency, energy efficiency, and yield efficiencies compared with any of Arco Chemical's previously built plants, all while maintaining high quality," he says.

Texaco also may have an edge in the marketplace by virtue of its peroxidation technology. When the company's propylene oxide and TBA facility in Port Neches, Tex., starts up in early 1994, it will enable Texaco to produce 400 million lb per year of propylene oxide and increase MTBE production from its current 4500 barrels per day to 19,500 bbl per day at Port Neches.

Now that Arco Chemical's basic patents on its peroxidation process have expired, some question whether Texaco's process is borrowed. A Texaco spokesman confirms that the company is employing a peroxidation process that yields propylene oxide and TBA coproducts, a process that in basic terms has long been used by Arco Chemical and other companies outside the U.S. But he adds that the process is "not identical to anyone else's process. It is our own proprietary process." Ralph S. Cunningham, Texaco Chemical president, says, "This project has additional importance because it uses technology that originated at Texaco Chemical's Austin [Texas] Research Laboratory. It is an example of developing proprietary technology to expand the company's product line."

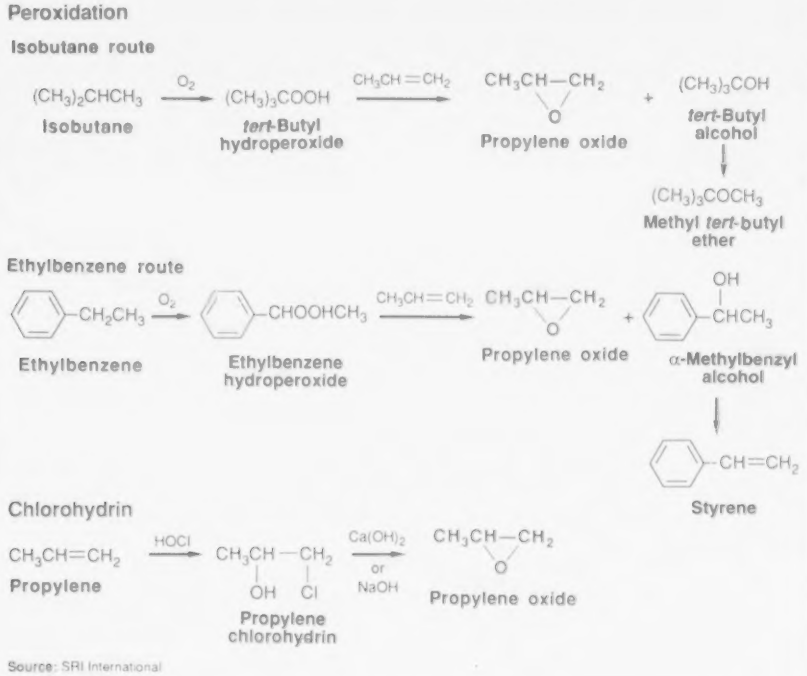
The expiration of basic patents on

Three firms will share U.S. market for propylene oxide

	Location	Annual capacity (millions of lb)	Basic process
Arco Chemical	Bayport, Tex.	1213	Peroxidation (isobutane)
	Channelview, Tex.	1100[a]	Peroxidation (ethylbenzene)
Dow Chemical	Freeport, Tex.	1100	Chlorohydrin
	Plaquemine, La.	450	Chlorohydrin
Texaco Chemical	Port Neches, Tex.	400[b]	Peroxidation (isobutane)

a Of this capacity, 500 million lb is slated to come on stream with a new unit in third quarter 1992. b Slated to start up in first quarter 1994.

Two major processes are used to produce propylene oxide



Source: SRI International

Arco Chemical's peroxidation process does not necessarily open the market up to all comers. Arco Chemical does not doubt that Texaco has done its own development work. The know-how necessary to operate a propylene oxide plant "goes way beyond what we put in a patent," says Lee. Taking technology from bench scale to commercial scale is complex, he adds, "and there are many safety and operating issues that you don't learn overnight. Anyone in an oxidation business can tell you that mixing hydrocarbons and oxygen is not without some inherent risk. With a number of years of operating experience, we have become more knowledgeable about how to operate. Besides, it is not a cheap technology to get into. I think that's one of the reasons we have held the position we have for a number of years."

Dow is likely to be hardest hit by the flood of new propylene oxide capacity, mainly because the processes used by Arco Chemical and the new Texaco plant provide significant cost advantages when the primary products, styrene and TBA, enjoy strong demand and pricing, says Petrocon's Horvath. "One major factor that may have influenced Texaco's decision to use the TBA process is the magnitude of the gasoline market, which will easily consume all of its TBA in making MTBE. So, propylene oxide may or may not be the driving force behind the new plants." By taking a cautious approach and not opting to add another propylene oxide plant, Dow will be in an awkward position in the near future, he says. "There's no room for another propylene oxide plant and there won't be for a long time unless Dow develops some breakthrough technology or replaces current chlorohydrin technology with a competitive peroxidation process."

Dow disagrees. David Naessens, product manager for polyurethane chemicals at Dow Plastics in Midland, Mich., says: "We don't see ourselves being at a great disadvantage. We obviously have done a lot of work looking at both of Arco Chemical's processes, and our conclusion is that after all of the depreciation of our plants, we are indeed competitive." In addition, he says, "unlike Arco Chemical and Texaco, we are not encumbered by coproducts. We run for propylene oxide economics alone."

Another plus on Dow's side is that the majority of the propylene oxide Dow makes is used internally. Texaco and Arco Chemical, he says, will have to rely more on merchant market sales. "Therefore, we will be running our plants at a higher rate of capacity." And he says Dow has not lost its chance to add capacity. Just last summer, Dow brought on a 200 million-lb-per-year expansion at Freeport and "we have another 400 million lb increment available to us there that we will bring on as the supply and demand balance dictates."

If Dow does modify its U.S. chlorohydrin process plants to use lime instead of caustic soda, the company will be more competitive with Arco Chemical on a cost basis, Horvath concedes. Lime, at roughly $50 per ton, is cost-effective compared with caustic soda, which trades at about $220 per ton. And the switch to lime would allow Dow to free up a significant amount of caustic soda to supply to merchant buyers without having to increase coproduct chlorine production.

Making the switch even more attractive, Dow is capable of producing its own lime. "Dow uses a lot of calcium carbonate and calcium chloride from sea shells in its magnesium process and it is very easy to convert calcium carbonate to calcium oxide, which is lime," Horvath adds. "In fact, Dow has drying furnaces at Freeport" that it can use to roast calcium carbonate limestone until all the carbon dioxide is driven off to make commercial calcium oxide, also known as caustic lime. "So it would be very easy for Dow to use that in a chlorohydrin process," Horvath conjectures. Naessens says that Dow has not yet decided to go with a lime process and that if it did, the company has many options for obtaining lime—and making its own is just one.

The switch is technically feasible; Dow already has propylene oxide facilities in Brazil and in Europe that use lime. What the company does have to ponder is the cost of converting its propylene oxide facilities at Freeport and Plaquemine, La., which would be considerable. The Freeport unit has pro-

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pylene oxide capacity for about 1.10 billion lb per year and the Plaquemine facility is rated at 450 million lb per year. "The earliest we would make a decision to implement the lime process would be around 1995 or 1996, and it will depend on the economics of propylene oxide, caustic, lime, and Dow Chemical as a whole," Naessens adds.

Using lime "is a very interesting way for Dow to use its basic raw material position to help its overall profitability and make it more competitive with Arco Chemical," adds Horvath.

Arco Chemical, like the other producers of propylene oxide in the U.S., wants to be well positioned to take advantage of increased demand for propylene oxide when the economy finally does recover, which Gist expects will happen in 1992. Arco Chemical anticipates the recession will end and that consump. n of propylene oxide will rebound. The c - clical forces that brought demand for these products down also will turn back up for companies that provide materials to the automotive and housing industries, the company believes.

Some of the propylene oxide from the new propylene oxide–styrene unit will be channeled toward supplying the urethane polyols business that Arco Chemical bought from Union Carbide in September 1991. The company was a major supplier to Carbide before the purchase. In addition, Arco Chemical says, it may tap the new plant to supply the 225 million-lb-per-year polyols plant at Channelview.

A part of the new capacity also may be used to supply growing outlets for propylene glycol. For example, some uses for ethylene glycol antifreeze have been converted to products based on propylene glycol, which has a lower toxicity profile. Ingestion of ethylene-glycol-based antifreeze is a commonly reported cause of poisoning in children and pets. Arco Chemical has very active programs both in the U.S. and in Europe to market propylene glycol to antifreeze formulators. In addition, it is touting propylene glycol's safety and environmental advantages over ethylene glycol in the deicers market. Aircraft deicing fluids have been based principally on this glycol, but now it has been listed as a hazardous air pollutant and the Clean Air Act has put pressure on airlines to find a substitute, says Lee. Arco Chemical has a propylene-glycol-based product for this end use, too. "We expect that both the aircraft deicing and antifreeze markets will give us significant new business and contribute to propylene oxide demand."

Arco Chemical is also involved in developing a number of other end uses for propylene oxide, including new derivative markets, says a spokesman. One example: the company's recent entry into the butanediol market. "We think that we are positioned to do that. We have the propylene oxide supply, we have the derivative capacity."

As for the coproduct styrene, "there will be factors that will affect how much styrene we produce." Principally, it will depend on demand for both propylene oxide and styrene. Arco Chemical can afford to be less concerned about that business. It has reduced its exposure to cyclicality in the styrene merchant market by signing on "equity partners" that have committed to a "significant portion of the styrene capacity of the new plant," says a spokesman. These unnamed partners will provide raw materials and pay their share of the plant operating costs, while not directly participating in the operation of the plant.

Arco Chemical believes, too, that the billion pounds of capacity for styrene that it is adding is only a small part of the world market for styrene, which totals 35 billion lb. "So in time [that capacity] will be absorbed by the demand in the marketplace," says Lee.

The export market is another viable outlet for Arco Chemical's propylene oxide and styrene. The company's worldwide production system allows it to take material from one location to another to meet demand until a new plant is built in that region. Given the cost involved in building one of these units, says Lee, "we don't want to make this investment all that often. So the flow of materials worldwide is something that we continually optimize."

Arco Chemical seems confident that its new plant, with its safety, environmental, and operating improvements, will be well equipped to meet the many market challenges it will face when it goes on stream later this year. Says Lee: "We have engineered and improved things incrementally over the past 25 years to the point where we have the most efficient system. There's no home run breakthrough in technology here, but I guess we've won the game by way of singles year after year [that were] accomplished by constantly improving our process."